



# Importance of the oxygen bond strength for catalytic activity in soot oxidation



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## ABSTRACT

The oxygen bond strength on a catalyst, as measured by the heat of oxygen chemisorption, is observed to be a very important parameter for the activity of the catalyst in soot oxidation. With both intimate contact between soot and catalyst (tight contact) and with the solids stirred loosely together (loose contact) the rate constants for a number of catalytic materials outline a volcano curve when plotted against their heats of oxygen chemisorption. However, the optima of the volcanoes correspond to different heats of chemisorption for the two contact situations. In both cases the activation energies for soot oxidation follow linear Brønsted-Evans-Polanyi relationships with the heat of oxygen chemisorption. Among the tested metal or metal oxide catalysts  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$  were nearest to the optimal bond strength in tight contact oxidation, while  $\text{Cr}_2\text{O}_3$  was nearest to the optimum in loose contact oxidation. The optimum of the volcano curve in loose contact is estimated to occur between the bond strengths of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Cr}_2\text{O}_3$ . Guided by an interpolation principle  $\text{Fe}_a\text{Cr}_b\text{O}_x$  binary oxides were tested, and the activity of these oxides was observed to pass through an optimum for an  $\text{FeCr}_2\text{O}_x$  binary oxide catalyst, which exhibited a rate constant at 550 °C that was 2.3 times higher than the one for pure  $\alpha\text{-Cr}_2\text{O}_3$  and 29 times higher than the one for pure  $\alpha\text{-Fe}_2\text{O}_3$ .

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## 1. Introduction

Soot particles in the exhaust from diesel vehicles are likely to cause lung cancer and to affect the climate both locally and globally [1–6]. The soot particles are therefore typically removed from the exhaust gas by filtration through a ceramic filter [7–9]. It is necessary with periodic regeneration of the filter, where the filter temperature is increased, and the soot is oxidized. The growing back pressure due to the soot deposits and the temperature increase required for filter regeneration are associated with increased fuel consumption [10]. To limit the increase in fuel consumption it is desirable to develop soot oxidation catalysts that can lower the regeneration temperature—ideally down to the typical temperature of the exhaust gas [7,11]. Here it is a challenge that the heterogeneously catalyzed soot oxidation is a gas/solid/solid interaction, where the contact between soot and catalyst is very important for the catalytic activity [12–14]. In tests, where soot and catalyst are crushed together (so-called tight contact), the oxidation occurs at a significantly lower temperature, than when soot and

catalyst are stirred together (so-called loose contact) [12–14]. TEM studies by Gardini et al [15] on Ag/soot mixtures have indicated that tight contact corresponds to an extensive interface between primary particles of catalyst and soot, whereas loose contact corresponds to fewer contact points at the interface between coagulates of catalyst particles and coagulates of soot particles. In several experiments [11,16–20] with oxidation of soot particles filtered from gas streams by a catalytic filter part of the soot oxidation has been observed to peak at a relatively low temperature in the range characteristic of tight contact with the catalyst, while another part of the soot oxidation has been observed to peak at a higher temperature more characteristic of loose contact with the catalyst. Hence an understanding of both tight and loose contact oxidation may be relevant for real filter applications.

To promote the development of improved catalysts that enable soot oxidation to take place at lower temperatures it is important to identify the parameters that determine the catalytic activity. The surface area of the employed catalyst is known to be of importance [21–23], but an improved understanding of the factors determining the intrinsic activity of a catalytic material would be beneficial. Borekov et al. [24] proposed that for metal oxide catalysts the oxygen bond strength on the catalyst surface, as measured by the heat of oxygen chemisorption, is a determining factor for activity

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in reactions involving oxygen activation. This has been observed to be the case in oxygen activation reactions such as  $^{16}\text{O}_2/^{18}\text{O}_2$  isotopic exchange [24] and oxidation of  $\text{CH}_4$  [24],  $\text{C}_3\text{H}_6$  [25],  $\text{H}_2$  [24–27] and  $\text{CO}$  [28–30]. The activity in the catalytic oxidation of  $\text{CO}$  on thin metal oxide films has also been correlated to the activation energy for oxygen desorption [31], which scales with the heat of chemisorption. Furthermore, the heat of chemisorption has also been found to be among the factors that play a role for the selectivity in oxidation of benzaldehyde [32] and methanol [33]. It is therefore relevant to investigate, if the heat of oxygen chemisorption can explain the trends in catalytic activity for soot oxidation, and that is the topic of the present work.

## 2. Materials and methods

### 2.1. Catalysts used for screening experiments

The catalysts used in the screening studies were bulk metals or metal oxides. In the cases of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Au}$ ,  $\text{Pd}$  and  $\text{Pt}$  commercially acquired samples were used. The suppliers and purities of the used samples are listed in Table S1 in the Supplementary information. In the cases of  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MnO}_x$ ,  $\text{ZnO}$ ,  $\text{CuO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  the oxide samples were prepared by flame spray pyrolysis according to the method described elsewhere [23]. This preparation method results in highly crystalline non-porous nanoparticles [34]. Catalyst precursors (Supplementary information, Table S2) at a total metal concentration of 0.25 M and 2-ethylhexanoic acid (Sigma Aldrich,  $\geq 99\%$ ) at a concentration of 1.0 M were dissolved in toluene (Sigma Aldrich, anhydrous,  $\geq 99.8\%$ ). The precursor solution was by means of a syringe pump delivered through a capillary (0.4 mm i.d.) into the flame at a rate of 3 mL/min, dispersed by a 5 NL/min  $\text{O}_2$  flow and ignited by an annular 1 NL/min  $\text{CH}_4$ , 3 NL/min  $\text{O}_2$  support flame (with NL referring to 298.15 K and 1 bar). The produced particles were with the aid of a vacuum pump collected on a water-cooled glass fiber filter (Whatman GF6,  $\varnothing = 240$  mm) 45 cm above the burner nozzle. The powder was then sieved to  $<600$   $\mu\text{m}$  in order to avoid the presence of filter fibers in the product. In the cases of the flame made chromium and manganese oxides the flame made samples were relatively amorphous, and prior to use the samples were calcined (2 h 500 °C, 10 °C/min) in order to convert samples into more crystalline materials identifiable by XRD.

### 2.2. $\text{SiO}_2$ supported Fe-Cr binary oxide catalyst

To investigate the properties of binary oxide catalysts a series of  $\text{SiO}_2$  supported  $\text{Fe}_x\text{Cr}_y\text{O}_z$  catalysts were prepared.  $\text{SiO}_2$  extrudates (Saint-Gobain, 250  $\text{m}^2/\text{g}$ ) were impregnated with an aqueous solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma Aldrich) to produce  $\text{Fe}_x\text{Cr}_y\text{O}_z/\text{SiO}_2$  with a total metal loading of 0.00278 mol/g (15 wt% metal for an  $\text{FeCrO}_x/\text{SiO}_2$  catalyst). The impregnated samples were aged for 2 h and then dried at 110 °C overnight. The dried catalyst precursors were then calcined in stagnant air for 2 h at 500 °C (ramp: 20 °C/min). Finally the calcined catalysts were crushed to  $<300$   $\mu\text{m}$  and then used in the powdered form.

### 2.3. Catalyst characterization

The specific surface areas of the catalyst samples were determined by nitrogen adsorption at liquid nitrogen temperature by means of a QuantaChrome Autosorb iQ<sub>2</sub> gas sorption analyzer. The specific surface area was determined through a 7-point, linear BET plot in the range of  $p/p_0 = 0.05\text{--}0.3$ . Prior to the BET measurement the sample was dried/degassed in flowing nitrogen at 170 °C for 2 h.

The identities of the various metal or metal oxide catalysts samples were verified by X-ray diffraction (XRD). XRD was measured with a PANalytical X'Pert PRO diffractometer with a Cu-K $\alpha$

X-ray source operated at 45 kV and 40 mA and with a Ni-filter and automatic anti-scatter and divergence slits. Diffractograms were recorded between  $2\theta = 10^\circ$  and  $2\theta = 80^\circ$  with a step width of  $2\theta = 0.0130^\circ$ .

### 2.4. Catalytic soot oxidation

The catalytic activity in soot oxidation was measured using a flow reactor setup. For the activity tests soot ( $\sim 2$  mg) and catalyst in a ratio of 1:5 (wt:wt) were stirred together with a spatula (loose contact) or crushed together for 6 min in an agate mortar (tight contact). In a few cases, where silica supported Fe-Cr binary oxide catalysts were tested, a higher soot:catalyst ratio of 1:10 (wt:wt) was used due to the lower fraction (15 wt%) of active material in these samples. The soot/catalyst mixture was transferred to a 7 cm long, 1 cm wide alumina sample holder, which was placed in the center of a quartz tube (length: 65 cm, inner diameter: 24 mm) within a horizontal, tubular furnace. The sample was then subjected to a 1 NL/min flow of 10.2 vol%  $\text{O}_2$  in  $\text{N}_2$ . The feed gases (technical grade  $\text{N}_2$  and  $\text{O}_2$  from AGA A/S) were dosed by means of Bronkhorst EL-FLOW mass flow controllers. When the sample had been installed in the oven, and once any remnants of air had been purged from the reactor (once the  $\text{CO}_2$  signal had fallen below the detection limit) the reactor was heated at a rate of 11 °C/min to a final temperature of 750 °C. The temperature was monitored by a type K thermoelement at the external surface of the quartz tube wall. The concentrations of  $\text{CO}$  and  $\text{CO}_2$  in the reactor effluent were monitored continuously using an ABB AO2020 IR gas analyzer calibrated using a certified  $\text{CO}/\text{CO}_2/\text{N}_2$  gas mixture from AGA A/S. During the experiments the levels of  $\text{CO}$  and  $\text{CO}_2$  in the effluent stream were in the 0–500 ppmv range, and the oxygen conversion was thus negligible in the present experiments. For that reason the oxygen concentration dependence was omitted in the kinetic analyses of the results.

The reactivity of diesel soot can vary widely with parameters such as the engine type [35], the fuel type [36,37], the engine load [38,39] and the presence of catalytically active ash species [40,41]. Numerous different types of soot are used in the oxidation studies in the literature, and the rate of catalytic soot oxidation scales with the inherent reactivity of the soot [23]. The soot used in the experiments was a reference material from NIST: “SRM 2975 Diesel Particulate Matter” (from an Industrial Forklift). Various characterizations of this carbonaceous material can be found in the literature [23,42–44].

### 2.5. Kinetic analysis

The results have been interpreted in terms of a global kinetic model fitted to the data across the full conversion range in the temperature programmed reaction tests:

$$\frac{dX}{dt} = k_{cat} \cdot (1 - X)^n + k_{non-cat} \cdot (1 - X)^n = A_{cat} \cdot \exp\left(\frac{-E_{a,cat}}{RT}\right) (1 - X)^n + A_{non-cat} \cdot \exp\left(\frac{-E_{a,non-cat}}{RT}\right) (1 - X)^n$$

where  $X$  is the degree of carbon conversion (obtained from numerical integration of the  $\text{CO}$  and  $\text{CO}_2$  signals),  $k$  is the rate constant,  $A$  is the pre-exponential factor,  $E_a$  is the apparent activation energy, and  $n$  is the reaction order in carbon. In this model the catalytic and the non-catalytic oxidation are treated as two parallel reactions. The kinetic parameters for the non-catalytic reaction, which are given the subscript “non-cat.” in the equation above, are determined from oxidation experiments in the absence of a catalyst. The reaction order in carbon was chosen to give the best fit to the data across all the tested samples (both loose and tight contact). The

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